

A high-quality x-ray scattering experiment on liquid water

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The structural investigation of water has a strong historical precedence, tracing roots at least as far back as Roentgen's early paper on the structure of water and the explanation of its density maximum. In principle, an accurate characterization of the molecular structure of liquid water can be found from solution scattering experiments. The structural information can be derived by back-Fourier transformation of the measured intensity curve as a function of the momentum transfer, Q , to give the molecular centers distribution function of water. Narten and Levy's [1] x-ray scattering studies and more recent neutron scattering experiments [2, 3] are commonly cited as the definitive sources for the molecular centers distribution function of the fluid at ambient conditions. Surprisingly, inconsistency exists among the measurements with respect to the oxygen-oxygen radial distribution function, $g_{oo}(r)$.

The inconsistency in the experimental results over the past 30 years have created a need to have an accurate measurement of water structure. We have reported a new, high-quality x-ray scattering experiment on pure ambient water using synchrotron beam line 7.3.3 at the ALS[4,5], using an experimental setup as shown in Figure 1. Several factors contribute to the improved quality of our intensity curves for pure water that have been unattainable in the past, including the use of a highly monochromatic source, a well characterized polarization correction, a Compton scattering correction that includes electron correlation's, and better resolved and more accurate intensities using a modern CCD detector. The error estimates of our data are smaller than the discrepancies between data sets collected in past x-ray experiments.

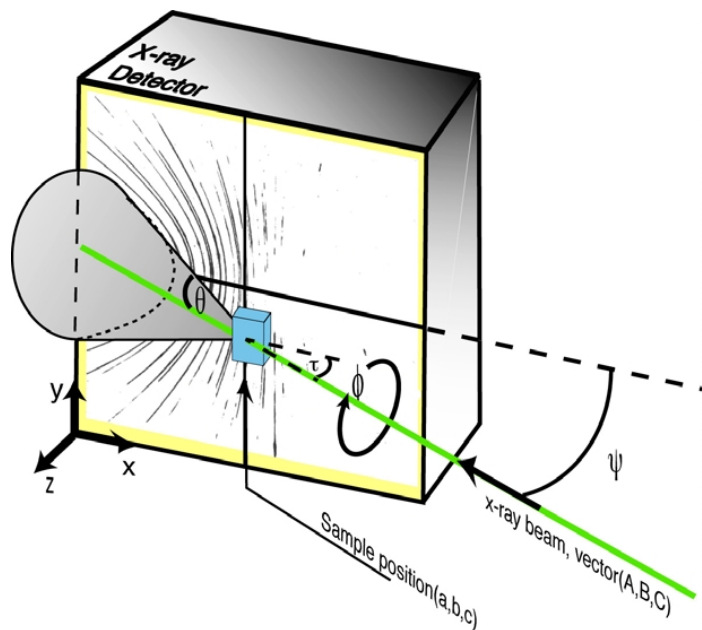


Figure 1. *Geometric set up of the sample and the detector at the Advanced Light Source. The detector was placed so that the plane defining the face of the detector intersected the incident x-ray beam at an angle of $\psi=27.8^\circ$. The sample holder was placed at an angle of $\tau=28^\circ$ to the x-ray beam. In the coordinate system of the face of the detector, the x-ray beam direction is defined as the unit vector (A, B, C) , and the sample position is the Cartesian point (a, b, c) , where a , b , and c are integer multiples of the detector pixel length of 82 micrometers. The setup allowed measurement of scattering over a range of θ from 3.0° to 113.0° degrees. The locus of points in ϕ (at constant θ) are expected to give the same value of the corrected intensity.*

In order to extract $g_{OO}(r)$ from the resulting intensity data required a theoretical modification surrounding the extraction of radial distribution functions from the x-ray scattering of molecular fluids. We propose a modification of the standard approach used for analyzing x-ray scattering to include the changes in the intramolecular electron distribution caused by chemical bonding effects. The modified atomic scattering factors that account for molecular bonding are used in the back-Fourier transform of the intensity curve to determine the radial distribution function.

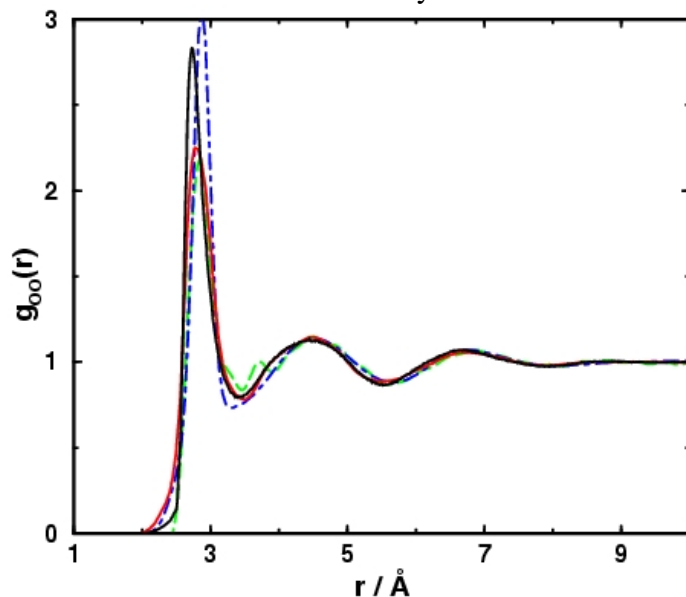


Figure 2. Comparison of current experimental $g_{OO}(r)$ with previous work. The ALS data [4,5], x-ray (black line); Narten and Levy [1], x-ray (dashed line); Soper and Philips [2] (dot-dashed line). Soper, Bruni, and Ricci, neutron [3] (gray line).

Figure 2 shows a comparison of our new oxygen-oxygen radial distribution function compared with the results of older experiments. We find a taller and sharper first peak, and systematic shifts in all peak positions to smaller r , relative to past reported $g_{OO}(r)$. Based on our experiments and theoretical analysis, we would argue that liquid water is more structured than that determined from past experiments. The implication for the highly accurate experimental and theoretical work on pure liquid water has been well-received by the simulation community in materials science and biology, and our data and analysis is making its way into other laboratories world-wide. We are currently analyzing data collected more recently at beam line 7.3.3. on water through-out the temperature range of 15-70°C. In the future we intend collect data on water at various pressures and through a greater range of temperatures.

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